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# Biogas crops grown in energy crop rotations: Linking chemical composition and methane production characteristics

Christiane Herrmann *, Christine Idler, Monika Heiermann

*Leibniz Institute for Agricultural Engineering Potsdam-Bornim, Max-Eyth-Allee 100, 14469 Potsdam, Germany*

## HIGHLIGHTS

- Methane formation characteristics from 405 silages of 43 crop species are presented.
- Silages from a wide range of crop species are well suited for biogas production.
- Besides lignin, products of silage fermentation significantly affect methane yield.
- The content of nitrogen-free extracts mainly determines methane contents.
- The fibre fraction has the largest impact on the rate of methane production.

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## ABSTRACT

Methane production characteristics and chemical composition of 405 silages from 43 different crop species were examined using uniform laboratory methods, with the aim to characterise a wide range of crop feedstocks from energy crop rotations and to identify main parameters that influence biomass quality for biogas production. Methane formation was analysed from chopped and over 90 days ensiled crop biomass in batch anaerobic digestion tests without further pre-treatment. Lignin content of crop biomass was found to be the most significant explanatory variable for specific methane yields while the methane content and methane production rates were mainly affected by the content of nitrogen-free extracts and neutral detergent fibre, respectively. The accumulation of butyric acid and alcohols during the ensiling process had significant impact on specific methane yields and methane contents of crop silages. It is proposed that products of silage fermentation should be considered when evaluating crop silages for biogas production.



## 1. Introduction

Biogas production via anaerobic digestion has become a well-established technology for renewable energy production in Europe. Several benefits of this process such as the reduction of greenhouse gas emissions, inactivation of pathogens, recycling of nutrients and the potential for flexible, demand-driven energy supply makes it a valuable means that contributes to the renewable energy mix and facilitates regional economic structures and employment in rural areas (Fröschle et al., 2015; Molinuevo-Salces et al., 2014; Zegada-Lizarazu and Monti, 2011). The anaerobic digestion process is capable of converting complex organic feedstock into methane, including agricultural by-products, organic wastes as well as animal manure and energy crops. The use of energy crops as feedstock in agricultural biogas plants is common in several European countries, mainly due to their high specific methane yields which makes the co-digestion of low-yielding animal manure feasible, and due to limited availability of industrial organic wastes (Herrmann and Rath, 2012; Nges et al., 2012). However, the production of energy crops is debatable since it requires agricultural land and can compete with food and feed supply. Furthermore, biogas production from energy crops largely concentrates on maize and the sustainability of maize-based biogas production is in question (Herrmann, 2013).

One important measure towards a sustainable biogas crop production would be the integration of energy crops in crop rotations. Crop rotations can provide versatile benefits such as the control of diseases, reduction of agrochemical and fertiliser input, reduced soil erosion, a more effective use of water and nutrients, lower economic and climatic risks, and higher biomass yields (Zegada-Lizarazu and Monti, 2011). Owing to the flexibility of the anaerobic digestion process in terms of feedstock conversion, opportunities

* Corresponding author. Tel.: +49 331 5699 231/211; fax: +49 331 5699 849.
*E-mail addresses:* cherrmann@atb-potsdam.de (C. Herrmann), cidler@atb-potsdam.de (C. Idler), mheiermann@atb-potsdam.de (M. Heiermann).

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are manifold: a large variety of different crop species can serve as biogas crops, which can be integrated in conventional cropping systems or can be part of multi-purpose cropping systems. They can be integrated as main crops, secondary crops for a second harvest after the main crop in double cropping systems, catch crops or perennial crops. For the adequate planning and design of crop rotations the knowledge of characteristics of a wide range of potential biogas crops is necessary. This regards effects on soil fertility and structure, on weed and disease control, and on biomass yields, but also knowledge about digestibility and methane production characteristics within the anaerobic digestion process is crucial. High methane yield potentials are desired for an efficient biogas production.

Several studies that analyse and compare the methane production potential of different crop species already exist (e.g. Amon et al., 2007; Dandikas et al., 2014; Gissén et al., 2014; Triolo et al., 2011). However, these studies investigate a comparatively low number of different crop species (usually less than 10). Different parameters have been reported to be correlated with the methane production potential of biomasses and several models have been developed for prediction of specific methane yields from biomasses. Promising correlations have previously been found for several chemical components such as acid detergent lignin (ADL), cellulose, acid detergent fibre (ADF), hemicellulose and crude fat (Dandikas et al., 2014; Gunaseelan, 2009; Rath et al., 2013; Triolo et al., 2011). However, correlation studies are usually either based on only few datasets (Dandikas et al., 2014; Triolo et al., 2011), mainly examine waste biomasses (Gunaseelan, 2009; Kafle and Kim, 2013), or focus on differences in methane yields within one crop species (Rath et al., 2013). Crops used as feedstock for biogas production are commonly harvested seasonally as whole crops, and are preserved for year-around supply to the anaerobic digestion plant by wet anaerobic storage via ensiling. It has been shown that ensiling can preserve the methane yield of crop biomass for up to one year or longer, yet the course and products of silage fermentation can significantly influence the specific methane yields of crop biomass (Herrmann et al., 2011). Nevertheless, parameters of ensiling, such as volatile fatty acids and alcohols, have not been included in correlation analyses in literature.

The novelty of the present study lies in that it is based on a comprehensive dataset obtained by the application of consistent methods of analyses and considers the ensiling process which is the typical method used to preserve seasonally harvested crop material for the year-around supply of biomass for biogas production. Analyses include 405 biogas silages from 43 different crops species, crop mixtures or positions within crop rotations (i.e. as main or secondary crop, or catch crop). The objective of the present study is to (1) characterise the chemical composition and methane formation of a wide range of crops grown in energy crop rotations under different agro-climatic conditions in Germany and preserved by ensiling; and (2) identify main chemical parameters that affect the methane production characteristics of biogas crop silages.

## 2. Methods

### 2.1. Description of raw materials

Crop material was obtained from energy crop rotations that were cultivated in field plot experiments at 8 different sites in Germany from the year 2005 to 2012 (Gödeke et al., 2007). An overview of crop species, location of cultivation, years and dates of harvest as well as the range of stages of maturity at harvest is given in Table 1. The experimental sites are further described in detail in Table S1 of the supplementary information. Directly after harvest of whole crops, crop materials were chopped to a particle length <20–30 mm and preserved by ensiling. If the dry matter (DM) content at harvest was estimated to lie below 25%, crop materials of annual grass and legume mixtures and forage cereals (catch crops) were wilted to a target DM content of 30–35% prior to chopping and ensiling.

### 2.2. Silage preparation

All crop materials investigated in the present study were preserved by ensiling. Crops were ensiled in 1.5 L glass silos (J. WECK GmbH u. Co. KG, Wehr, Germany) immediately after chopping. Chopped crop materials were pressed into the glass jars with a manually operated plunger. All silos were filled completely leaving no headspace in the jars, and were subsequently sealed airtight. A glass lid, rubber ring and four metal clamps were used to close the silos in a way which prevented air from infiltrating into the silo but allowed gases formed during ensiling to escape. Silos were stored at 25 °C for a storage period of 90 days. Ensiling in this study was generally conducted without silage additives. Silages were prepared in triplicate or quadruplicate for each variant.

### 2.3. Chemical analyses

After taken out of the silos, ensiled crop materials were immediately frozen and stored at −18 °C before they were further processed for analyses of chemical composition and methane production. DM and organic dry matter (ODM) content were measured by oven drying at 105 °C and ashing of the dried sample at 550 °C according to standard procedures (VDLUFA, 2006). The pH-value of the silages was determined using a measuring electrode Sen Tix 41 (WTW, Weilheim, Germany). Lactic acid, volatile fatty acids and alcohols were measured in cold water extracts of the silages. A high performance liquid chromatograph (Dionex, Sunnyvale, USA) equipped with an Eurokat H column (Knauer, Berlin, Germany) and refractive index detector was applied for analyses of lactic acid. Analyses of volatile fatty acids (acetic, propionic, n-butyric, iso-butyric, n-valeric, iso-valeric and n-caproic acid) and alcohols (ethanol, propanol, 1,2-propanediol, 2,3-butanediol) were conducted using a gas chromatograph (Agilent Technologies Inc., Santa Clara, CA, USA) equipped with a PERMABOND® FFAP capillary column (Machery-Nagel GmbH & Co KG, Düren, Germany) and a flame ionisation detector. The DM content of the silages was corrected for losses of organic acids and alcohols during oven drying, as suggested by Weißbach and Kuhla (1995). All parameters that are based on DM, refer to the corrected DM content.

Crude fat, crude fibre, neutral detergent fibre (NDF), ADF and ADL were analysed as described in detail previously (Herrmann et al., 2011, 2014), using the Ankom$^{XT10}$-Extractor (Ankom Technology Corp., Macedon NY, USA) for crude fat and the Ankom$^{2000}$ Fibre Analyser system and filter bag technology (Ankom Technology Corp., Macedon, NY, USA) for fibre analyses. Elemental carbon and nitrogen were detected with an elemental analyser (vario EL, Elementar Analysensysteme GmbH, Hanau, Germany), applying the DUMAS combustion method (VDLUFA, 2006). Crude protein was calculated as 6.25 times the elemental nitrogen content. The C/N ratio of silages was calculated as the elemental carbon content divided by the elemental nitrogen content. Nitrogen-free extracts were obtained by subtracting the crude protein, crude fibre, crude fat and crude ash content from $100\%_{DM}$. The cellulose content is represented by the difference between ADF and ADL, and the hemicellulose content is represented by the difference between NDF and ADF.

### 2.4. Batch anaerobic digestion test

Biogas production characteristics including specific methane yields of silages and the quality of the produced biogas were